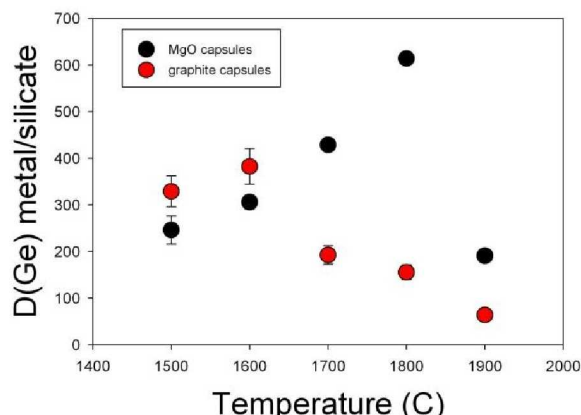


**Determining the metal/silicate partition coefficient of Germanium: Implications for core and mantle differentiation.** C. King<sup>1,2</sup>, K. Richter<sup>3</sup>, L. Danielson<sup>3</sup>, K. Pando<sup>3</sup>, C. Lee<sup>4</sup> <sup>1</sup>Dept. Geosciences, Univ. Arizona, Tucson, AZ, 85721; <sup>2</sup>Lunar and Planetary Institute, Houston, TX, 77058; <sup>3</sup>Johnson Space Center, Houston, TX, 77058; <sup>4</sup>Dept. Earth Science, Rice University, Houston, TX, 77005

**Introduction:** Currently there are several hypotheses for the thermal state of the early Earth. Some hypothesize a shallow magma ocean [1], or deep magma ocean [2], or heterogeneous accretion which requires no magma ocean at all [3]. Previous models are unable to account for Ge depletion in Earth's mantle relative to CI chondrites (e.g., [3]). In this study, the element Ge is used to observe the way siderophile elements partition into the metallic core [1]. The purpose of this research is to provide new data for Ge and to further test these models for Earth's early stages.

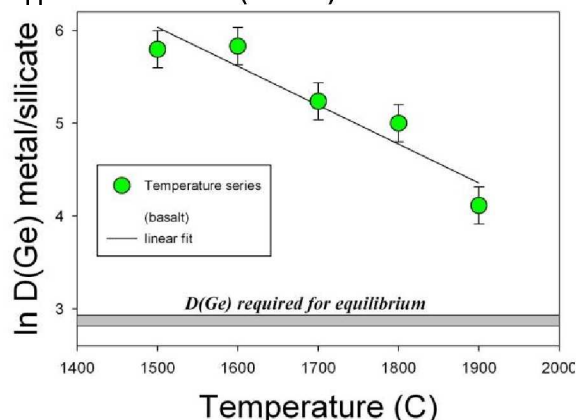
The partition coefficients ( $D_{\text{Ge}} = c_{\text{metal}}/c_{\text{silicate}}$ , where  $D$  = partition coefficient of Ge and  $c$  = concentration of Ge in the metal and silicate, respectively) of siderophile elements were studied by performing series of high pressure, high temperature experiments. They are also dependent on oxygen fugacity, and metal and silicate composition. Ge is a moderately siderophile element found in both the mantle and core, and has yet to be studied systematically at high temperatures. Moreover, previous work has been limited by the low solubility of Ge in silicate melts (< 100 ppm and close to detection limits for electron microprobe analysis). Reported here are results from 14 experiments studying the partitioning of Ge between silicate and metallic liquids. The Ge concentrations were then analyzed using Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS) which is sensitive enough to detect ppm levels of Ge in the silicate melt.

**Procedures:** The sample used for these experiments was a powder containing 70 wt.% Knippa Basalt, composition [4], and 30 wt.% Fe, Ge mixture (95 wt.% Fe and 5 wt.% Ge). Two different capsules were used: MgO and graphite. All experiments were performed using a piston cylinder apparatus at constant pressure of 1.0 GPa. Once the samples were brought under pressure, they were heated to temperatures of 1500 – 1900 °C, high enough to attain equilibrium and were heated for durations based on diffusion times across capsule distance ([5], [6]). A time series of four experiments at 1600 °C was conducted as a test for approach to equilibrium. The temperature was measured using Type C thermocouple (W-Re) wires with an accuracy of  $\pm 2$  °C. Samples were quenched by turning off the power and keeping constant pressure until the temperature reached 100 °C.



**Figure 1:** Results of MgO and graphite capsule series experiments. The lack of clear trends is due to slightly different oxygen fugacity and melt composition between each experiment. Corrected values which allow better comparison are made below.

**Analysis:** All samples were analyzed for major element composition using a Cameca SX100 for electron microprobe analysis (EMPA) at NASA-JSC (10  $\mu\text{m}$  beam at 15 kV and 10 nA). MgO capsules reacted with the silicate melt to produce increasingly magnesian melts at higher temperatures (37 wt% MgO at 1900 °C). Metal in the graphite capsules contains 5-6 wt% C, consistent with the Fe-C phase diagram [7]. Ge content of the glasses was lower than detection limits of EMPA, therefore, samples were analyzed for trace elements using LA-ICP-MS at Rice University. Standards used for the laser analysis were BHVO2g, BCR2g, BIR1g glasses. Analyses in medium resolution mode were carried out and  $^{74}\text{Ge}$  was normalized to  $^{25}\text{Mg}$  to calculate Ge in ppm in the silicates (Table 1).



**Figure 2:**  $\ln D(\text{Ge})$  versus temperature for the graphite capsule series. A linear fit to the data shows a close to factor of 10 decrease across 400 °C.

**Results:** Partition coefficients were calculated for each of the two temperature series (Fig. 1). The samples in MgO capsules show a general increase of  $D_{\text{Ge}}$  as temperature increases while the graphite samples show a decrease of  $D_{\text{Ge}}$  as temperature increases. For each sample  $f\text{O}_2$  was calculated relative to the iron-wüstite buffer (IW) according to the approximation:  $-2 \cdot \log[X_{\text{Fe}}/X_{\text{FeO}}]$ .

**Discussion:** The effect of temperature on  $D(\text{Ge})$  can be determined for the graphite capsule series in which pressure, silicate and metallic melt composition are constant and a small correction can be made assuming the valence of Ge is 4+. After this small correction is applied, it is clear that  $D(\text{Ge})$  met/sil decreases by a factor of nearly 10 from 1500 to 1900 °C (Fig. 2). This decrease is in agreement with the few constraints from previous work [8, 9].

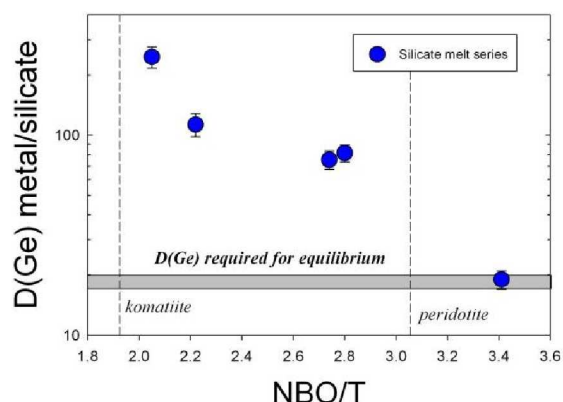
The effect of silicate melt composition on  $D(\text{Ge})$  can be determined from the MgO series in which pressure and metallic melt composition is constant, and correction can be made for  $f\text{O}_2$  and temperature (from the graphite series). The resulting trend indicates that  $D(\text{Ge})$  met/sil decreases from magnesian basalt (NBO/T = 2.1) to peridotite (NBO/T = 3.4) [10].

**Implications for early Earth:** If Ge in the Earth's mantle was set by early metal silicate equilibrium, we can estimate the  $D(\text{Ge})$  required. We assumed the bulk composition for early Earth is roughly the same as CI carbonaceous chondrites (32 ppm), core = 32 mass%, and mantle = 68 mass%. Using these assumptions, and correcting for Ge volatility according to McDonough and Sun [11] results in  $D_{\text{Ge}} = 18$  (Figs. 2 and 3).

It is clear that  $D(\text{Ge})$  approaches this value at temperatures near 2000 °C and peridotite melt. Our new findings, combined with the known effect of S on decreasing  $D_{\text{Ge}}$  [9,12], indicate that a shallow

magma ocean could indeed explain the Ge concentrations in the mantle, and excessively high temperatures are not required. The effect of pressure has not been studied yet, but should also be considered in any explanation for Ge.

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**Figure 3:**  $D(\text{Ge})$  vs. NBO/T – the degree of melt depolymerization- for the MgO capsule series.  $D(\text{Ge})$  is lowered substantially in peridotite melts.  $D(\text{Ge})$  has been corrected for temperature and  $f\text{O}_2$  to isolate the effect of melt composition alone.

**Table 1:** Summary of experiments in this study performed at 1.0 GPa. Two different series were performed – two temperature series each with a different capsule (MgO and graphite), from 1500 to 1900 °C.

Run Label	Temperature	Duration (mins)	Capsule
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